

## Demixing in binary mixtures of hard hyperspheres

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**Abstract.** – The phase behavior of binary fluid mixtures of hard hyperspheres in four and five dimensions is investigated. Spinodal instability is found by using a recent and accurate prescription for the equation of state of the mixture that requires the equation of state of the single component fluid as input. The role played by the dimensionality on the possible metastability of the demixing transition with respect to a fluid-solid transition is discussed. The binodal curves in the pressure–chemical potential representation are seen to lie on a common line, independent of the size ratio.

The phase diagram of the simplest model of a binary mixture, that of additive hard spheres, has not been completely determined up to now and remains as an interesting open problem. Ever since the solution of the Ornstein-Zernike equation with the Rogers-Young closure for such a mixture given by Biben and Hansen [1], the until then widespread and unchallenged belief that these mixtures cannot phase separate into two fluid phases (which was supported by the analytical results of the Percus-Yevick approximation [2]) has been seriously questioned. In fact, a wealth of papers dealing with this and related demixing problems have recently appeared in the literature [3–8], but the issue is still far from being settled. One of the key aspects of this fluid-fluid transition in hard-sphere mixtures is that, if it exists at all, it must be entropy driven. In contrast, in other mixtures such as molecular mixtures, the transition is driven by an asymmetry between the like- and unlike-particle interactions, i.e. it is energy driven, and at least the qualitative phase behavior is rather well characterized [9].

Entropy driven demixing was nicely shown by Frenkel and Louis to occur in a simple lattice model for a binary hard-core mixture [3]. Experimental work has provided evidence that results for (asymmetric in size) hard-sphere mixtures approximate rather well the thermodynamic properties of real colloidal systems, so it has been suggested that a likely physical mechanism behind the entropy driven demixing transition is osmotic depletion. This notion, first introduced to explain phase separation in polymer-colloid mixtures, is included in the scaled particle theory of Lekkerkerker and Stroobants [4], which predicts a fluid-fluid spinodal

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instability for highly asymmetric mixtures but whose domain of validity is not clear yet. The depletion picture is also present in other more recent studies [5, 8].

A different approach to the demixing problem relies on the use of equations of state (EOS) for the hard-sphere mixture. It is well known that the popular Boublík-Mansoori-Carnahan-Starling-Leland (BMCSL) EOS of state [10] does predict no demixing. On the other hand, Coussaert and Baus [6] have proposed an alternative EOS with improved virial behavior that predicts a fluid-fluid transition but at such high pressures that it is argued to be metastable with respect to a stable fluid-solid transition. In this Letter we also take the EOS approach for binary mixtures of hard additive *hyperspheres*. By looking into the higher dimensionality, one can gain insight into any thermodynamic phenomenology that extends to such dimensionality [11]. We will show that indeed these systems clearly exhibit a spinodal instability behavior.

Let us consider an  $N$ -component mixture of (additive) hard spheres in  $d$  dimensions. The total number density is  $\rho$ , the set of molar fractions is  $\{x_i\}$ , and the set of diameters is  $\{\sigma_i\}$ . The packing fraction is  $\eta = \sum_{i=1}^N \eta_i = v_d \rho \langle \sigma^d \rangle$ , where  $\eta_i = v_d \rho_i \sigma_i^d$  is the partial packing fraction due to species  $i$ ,  $\rho_i = \rho x_i$  is the partial number density corresponding to species  $i$ ,  $v_d = (\pi/4)^{d/2} / \Gamma(1 + d/2)$  is the volume of a  $d$ -dimensional sphere of unit diameter, and  $\langle \sigma^n \rangle \equiv \sum_{i=1}^N x_i \sigma_i^n$ . In previous work [12] we have proposed a *simple* EOS for the mixture,  $Z_m(\eta)$ , consistent with a given EOS for a single component system,  $Z_s(\eta)$ , where  $Z = p / \rho k_B T$  is the compressibility factor,  $p$  being the pressure,  $T$  the absolute temperature and  $k_B$  the Boltzmann constant. Our EOS reads

$$Z_m(\eta) = 1 + [Z_s(\eta) - 1] 2^{1-d} \Delta_0 + \frac{\eta}{1 - \eta} \left[ 1 - \Delta_0 + \frac{1}{2} \Delta_1 \right], \quad (1)$$

$$\Delta_p \equiv \frac{\langle \sigma^{d+p-1} \rangle}{\langle \sigma^d \rangle^2} \sum_{n=p}^{d-1} \binom{d+p-1}{n} \langle \sigma^{n-p+1} \rangle \langle \sigma^{d-n} \rangle. \quad (2)$$

In the one-dimensional case, eq. (1) yields the *exact* result  $Z_m(\eta) = Z_s(\eta)$ . Further, for  $d = 2$  and 3, it proved to be very satisfactory when a reasonably accurate  $Z_s(\eta)$  was taken [12, 13]. In all instances examined with different  $Z_s(\eta)$ , however, no demixing is found for the resulting EOS for the mixture in these dimensionalities.

One-component fluids of hard hyperspheres ( $d \geq 4$ ) have attracted the attention of a number of researchers over the last twenty years [11, 14–18]. Amongst other similarities, they share the property of hard disks and spheres of exhibiting a first order freezing transition. This transition occurs at a packing fraction  $\eta_f$  that, relative to the close-packing fraction  $\eta_{cp}$ , decreases monotonically with increasing  $d$ . Perhaps the most accurate proposals to date for  $Z_s(\eta)$  in  $d = 4$  and  $d = 5$  are the semiempirical EOS proposed by Luban and Michels [15]:

$$Z_s(\eta) = 1 + b_2 \eta \frac{1 + [b_3/b_2 - \zeta(\eta) b_4/b_3] \eta}{1 - \zeta(\eta) (b_4/b_3) \eta + [\zeta(\eta) - 1] (b_4/b_2) \eta^2}, \quad (3)$$

where  $b_n$  are (reduced) virial coefficients defined by the series  $Z_s(\eta) = 1 + \sum_{n=1}^{\infty} b_{n+1} \eta^n$ . Equation (3) is consistent with the (known) exact first four virial coefficients, regardless of the choice of  $\zeta(\eta)$ . Luban and Michels observed that the computer simulation data favor a *linear* approximation for  $\zeta(\eta)$  and by a least-squares fit procedure found  $\zeta(\eta) = 1.2973(59) - 0.062(13) \eta / \eta_{cp}$  for  $d = 4$  and  $\zeta(\eta) = 1.074(16) + 0.163(45) \eta / \eta_{cp}$  for  $d = 5$ . Substitution of eq. (3), using the above linear fits for  $\zeta(\eta)$ , into eq. (1) produces the EOS of a mixture of hard additive hyperspheres in  $d = 4$  and  $d = 5$  dimensions, respectively. These EOS are the basis of our subsequent analysis. As an illustration of the accuracy of our EOS, in Fig.

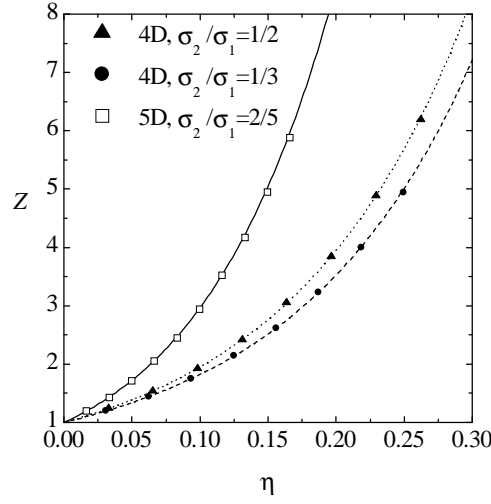


Fig. 1 – Compressibility factor for three equimolar mixtures in 4D and 5D systems. Lines are the theoretical results and symbols are computer simulation data [19].

1 we display the comparison of the density dependence of  $Z_m(\eta)$  as obtained in this work with the results of computer simulation [19] for three equimolar binary mixtures and different values of the diameter ratio  $\alpha \equiv \sigma_2/\sigma_1$ , both in 4D and 5D. As clearly seen in the figure, the agreement is virtually perfect. This agreement has been amply confirmed for other values of the concentration  $x_1$  and the diameter ratio  $\alpha$  [19].

We next consider the instability of a binary mixture ( $N = 2$ ) by looking at the Helmholtz free energy per unit volume,  $a$ , which is given by

$$\frac{a}{\rho k_B T} = -1 + \sum_{i=1}^2 x_i \ln(\rho_i \lambda_i^d) + \int_0^\eta \frac{d\eta'}{\eta'} [Z_m(\eta') - 1], \quad (4)$$

where  $\lambda_i$  is the thermal de Broglie wavelength of species  $i$ . We locate the spinodals through the condition  $a_{11}a_{22} - a_{12}^2 = 0$ , with  $a_{ij} \equiv \partial^2 a / \partial \rho_i \partial \rho_j$ . Due to the spinodal instability, the mixture separates into two phases of different composition. The coexistence conditions are determined through the equality of the pressure  $p$  and the two chemical potentials  $\mu_1$  and  $\mu_2$  in both phases ( $\mu_i = \partial a / \partial \rho_i$ ), leading to binodal curves. It should be noted that in our calculations we have considered the range  $\eta_1 + \eta_2 \leq \eta_{cp}$  ( $\eta_{cp} = \pi^2/16 \simeq 0.617$  in 4D and  $\eta_{cp} = \pi^2\sqrt{2}/30 \simeq 0.465$  in 5D [15]) and that without loss of generality we have set  $k_B T = 1$ . Also, for future reference it is useful to recall that the freezing transition in the same systems occurs at a packing fraction  $\eta_f \simeq 0.31$  and  $\eta_f \simeq 0.20$ , respectively [16].

Figures 2 and 3 show the results for the spinodals and binodals in the  $\eta_2$  vs  $\eta_1$  plane and for the binodals in the  $p\sigma_1^d$  vs  $\eta_1$  plane for different values of  $\alpha$  and for  $d = 4$  and  $d = 5$ , respectively. The location of the critical point tends to go down and to the right in the  $\eta_2$  vs  $\eta_1$  plane as  $\alpha$  decreases. Also, in both dimensionalities and for a given  $\alpha$ , the binodal and spinodal curves become practically indistinguishable to the right of the critical point. In contrast, while the binodals with the bigger  $\alpha$  are always above those corresponding to a lower diameter ratio, to the left of the critical point the different spinodal curves cross each other for  $d = 4$ . The value of the critical pressure  $p_c$  (in units of  $\sigma_1^{-d}$ ) is not a monotonic function

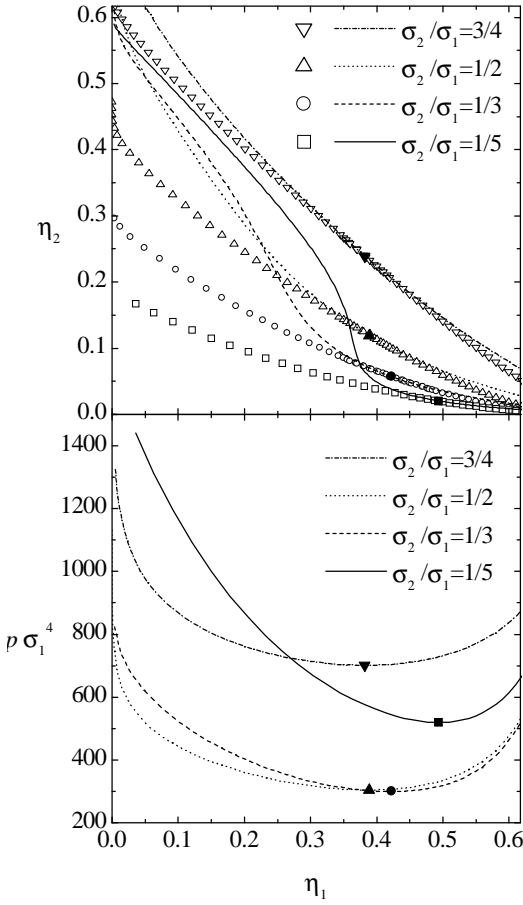


Fig. 2

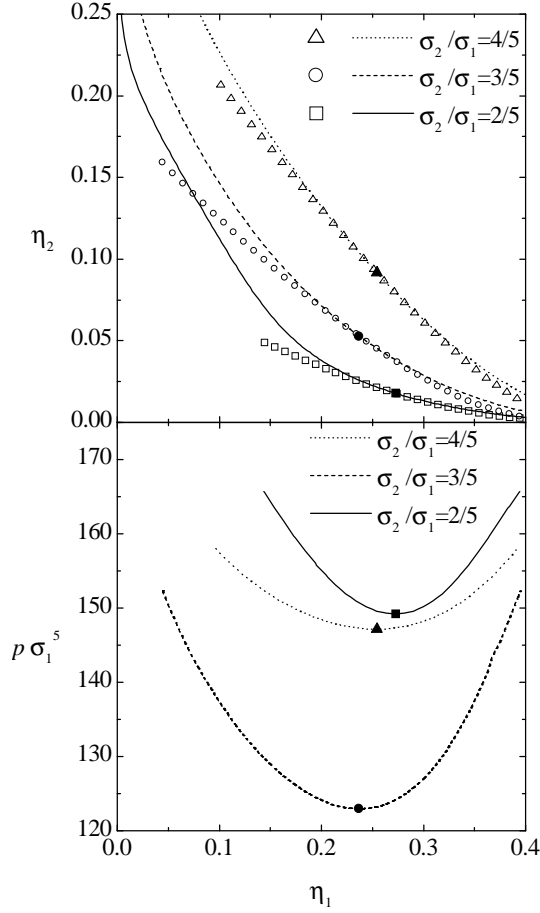


Fig. 3

Fig. 2 – Spinodal curves (upper panel: lines) and binodal curves (upper panel: symbols; lower panel: lines) in a 4D system. The filled symbols are the critical consolute points.

Fig. 3 – Same as Fig. 2, but for a 5D system.

of  $\alpha$ ; its minimum value lies between  $\alpha = 1/3$  and  $\alpha = 1/2$  when  $d = 4$ , and it is around  $\alpha = 3/5$  for  $d = 5$ . This non-monotonic behavior was also observed for hard spheres [6].

It is conceivable that the demixing transition in binary mixtures of hard hyperspheres in four and five dimensions described above may be metastable with respect to a fluid-solid transition (cf. the values of  $\eta_f$ ), as it also occurred with the case of hard spheres [6]. In fact the value of the pressure at the freezing transition for the single component fluid is  $p_f \sigma^d \simeq 12.7$  ( $d = 3$ ), 11.5 ( $d = 4$ ), and 12.2 ( $d = 5$ ), i.e.  $p_f \sigma^d$  does not change appreciably with the dimensionality but is clearly very small in comparison with the critical pressures  $p_c \sigma_1^d$  we obtain for the mixture; for instance,  $p_c \sigma_1^d \simeq 1000$  ( $d = 3$ ,  $\alpha = 3/10$ ) [6], 300 ( $d = 4$ ,  $\alpha = 1/3$ ), and 123 ( $d = 5$ ,  $\alpha = 3/5$ ). However, one should also bear in mind that, if the concentration  $x_1$  of the bigger spheres decreases, the value of the pressure at which the solid-fluid transition in the mixture occurs in 3D is also considerably increased with respect to  $p_f$  (cf. Fig. 6 of

Ref. [6]). Thus, for concentrations  $x_1 \simeq 0.01$  corresponding to the critical point of the fluid-fluid transition, the maximum pressure of the fluid phase greatly exceeds  $p_f$ . If a similar trend with composition also holds in 4D and 5D, and given that the critical pressures become smaller as the dimensionality  $d$  is increased, it is not clear whether the competition between the fluid-solid and the fluid-fluid transitions in these dimensionalities will always be won by the former. The point clearly deserves further investigation.

An interesting feature arising in our results, and which to our knowledge has not been discussed up to now, must be mentioned. There is a remarkable similarity between the binodal curves represented in the  $p\sigma_i^d-\eta_1$  and in the  $\mu_i-\eta_1$  planes (not shown). By eliminating  $\eta_1$  as if it were a parameter, one can represent the binodal curves in a  $\mu_i$  vs  $p\sigma_i^d$  plane. This is shown in Figs. 4 and 5, where we have chosen the origin of the chemical potentials such as to make  $\lambda_i = \sigma_i$ . The binodals in the  $\mu_1-p\sigma_1^d$  plane collapse into a single universal curve (which is in fact almost a straight line) for each dimensionality ( $d = 3$ ,  $d = 4$ , and  $d = 5$ ). We have obtained the data for  $d = 3$  by using the EOS due to Coussaert and Baus [6]. For each dimensionality, the curve  $\mu_1 = F_1(p\sigma_1^d)$  is seen to be independent of the asymmetry in sizes as the contributions from each  $\alpha$  to a portion of the curve overlap. Something similar occurs with the curve  $\mu_2 = F_2(p\sigma_2^d)$  and the calculations indicate that  $F_1 = F_2$  in the sense that if plotted on the same plane, both curves seem to probe different regions of the plane but otherwise overlap reasonably well. This is illustrated by Fig. 5 for the case  $d = 4$ , where the points of  $\mu_2$  corresponding to  $\alpha = 3/4$  connect with those of  $\mu_1$  for  $\alpha = 1/3$  and  $\alpha = 1/2$ . These properties could reveal the existence of a certain *geometrical* regularity that might characterize the entropy driven transitions. One could then state that all binary hard (hyper)sphere mixtures belong to the same *universality class* since, for fixed  $d$ , there are some properties such as the binodal curves in which the asymmetry is to a certain extent irrelevant. We also find an upper quasi-universality: for the range of common values, the universal curve in 3D lies close but somewhat above the universal curve in 4D, and in turn this latter lies above the one in 5D (note, however, that the origin of  $\mu_i$  is actually a matter of choice). All three curves approach straight lines of slopes 0.44 ( $d = 3$ ), 0.45 ( $d = 4$ ), and 0.43 ( $d = 5$ ) in the region of their higher values.

The results presented in this Letter confirm that the geometrical effects of osmotic depletion become more important as the dimensionality increases in much the same way that in 3D they are more important for parallel hard cubes than for hard spheres. It could be argued that the results we have presented so far (except for the universality, which is also found with a completely independent EOS in 3D) strongly depend on our prescription (1) for the EOS of the mixture and on the use of eq. (3). To address the first point, we have carried out calculations using the van der Waals one-fluid theory with the Luban-Michels EOS in 4D and found no spinodal instability for  $\eta_1 + \eta_2 \leq \eta_{cp}$ . Concerning the second point, we have also performed calculations using Eq. (1) for  $Z_m(\eta)$  with the EOS proposed by Baus and Colot [17] for the single component fluid. In this instance we also find spinodal curves which do not coincide but are qualitatively similar with the ones obtained using eq. (3). The sensitivity of the spinodal curves with respect to the EOS was also noted in the case of hard spheres [6]. Finally, we want to mention that our approach opens up the possibility of examining whether there is a critical dimension above which the fluid-fluid transition in hard hypersphere mixtures becomes stable, including the role that the asymmetry plays in it. Also we hope that the universal feature that we have described will stimulate other studies to clarify its physical origin and further implications.

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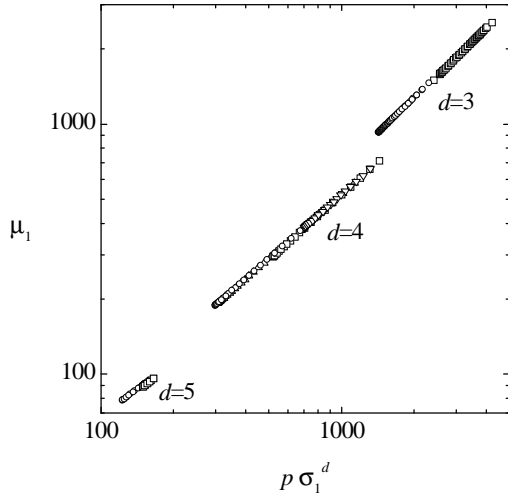


Fig. 4

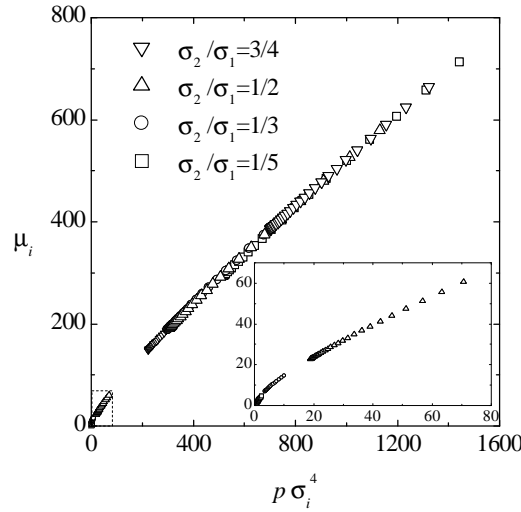


Fig. 5

Fig. 4 – Binodal curves in the  $\mu_1$  vs  $p\sigma_1^d$  plane for  $d = 3$  (circles:  $\sigma_2/\sigma_1 = 1/5$ , squares:  $\sigma_2/\sigma_1 = 1/10$ ),  $d = 4$  (symbols as in Fig. 2), and  $d = 5$  (symbols as in Fig. 3). Note that for each size ratio the binodal curve is restricted to  $p \geq p_c$ .

Fig. 5 – Binodal curves in the  $\mu_i$  vs  $p\sigma_i^4$  plane for a 4D system. The case  $i = 1$  corresponds to  $\mu_i \gtrsim 200$  and is represented by the large symbols, while the case  $i = 2$  corresponds to  $\mu_i \lesssim 200$  and is represented by the small symbols. The inset is a magnification of the box enclosed by the dashed lines and shows  $\mu_2$  vs  $p\sigma_2^4$  for  $\sigma_2/\sigma_1 = 1/2, 1/3$  and  $1/5$ .

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